Phase Diagram and Thermophysical Properties of Superheated Fluids

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Thermophysical properties of a liquid, such as thermal conductivity and thermal diffusivity, are usually measured for samples in stable states. These states are characterized by long (infinite) life times. The region above the stability boundary has been poorly investigated so far. At the same time the observation of the metastable states is the common in thermophysics of pulse action on a condensed matter. The aims of our work were determination of the mean life time of a superheated liquid at a given temperature and pressure before its spontaneous boiling-up; and investigation of thermophysical properties of fluids in short-lived states – superheated with respect to the liquid-vapor equilibrium temperature and/or to the temperature of thermal decomposition of molecules in quasi-static process. The objects of our studies were polymeric liquids (as typical thermally unstable systems) and gas-saturated liquids (as systems with extended metastable region). An investigation of the properties of a short-lived system requires the development of high-speed techniques of heating the sample microvolume. Our approach is based on application of the high-temperature equation of state taking into account decomposition of a polymer, the procedures of automatic choice of heating function for thin wire probe, the monitoring of a phase stability boundary of a reacting system by the characteristic break on the time dependence of the heat flux from the probe, and the calculation of thermophysical properties of superheated liquids from the data of pulse experiment and the model of the process [1-3]. The set of experimental data on spontaneous boiling-up temperature as a function of pressure and the heating path is expected to clarify the high-temperature part of the phase diagram inaccessible for quasi-static measurements. In particular, the approximations for the spinodal and the critical point have been obtained from these data. In the case of polymers which cannot form the vapor phase without their decomposition we have observed the reproducible process of boiling-up of low-molecular-weight products formed in the course of pulse heating. Using the regime of thermostabilization of the pulse-heated probe, the coefficients of thermal conductivity and thermal diffusivity for locally superheated substances have been determined over a wide range of temperature. Generally, the approach provides a basis for elucidation of the relation between thermophysical properties of some "unconventional fluids" [4] and the type of their phase diagram.

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